

Determination of Hydronium Ion
in Jarosite-Type Compounds

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Final Report

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Introduction

The identification of materials can be obtained by the use of many modern methods. One of these techniques is Infra red absorption spectroscopy. The first utilization is to qualitatively identify the unknown material by its unique spectrum. Once the initial analysis is complete, (general spectral features) one must assign the individual spectral bands to the appropriate molecular vibration in order to make a positive identification of the specific material. After a complete description of the spectral features is obtained, one can use chosen vibrational bands for quantitative information of the sample. The present contract uses the above technique to determine the amount of hydronium in Jarosite minerals. The outline of the work completed is stated in the following "Statement of Work".

- 1 - CANMET will supply several "end-member" jarosite compounds (sodium, potassium, rubidium, silver, thallium, hydronium, ammonium, lead and mercury) which are suspected to contain hydronium ion concentrations. One or two natural jarosites will also be provided.
- 2 - The presence of hydronium ion in the above compounds will be confirmed and quantified by both low-temperature i.r. spectroscopy and Laser Raman spectroscopy. Relevant hydronium standards will be obtained by the University.
- 3 - CANMET will prepare and analyze (M^+ , Fe, SO_4 , wt loss) several series of alkali-hydronium jarosites and Pb-Cu-hydronium jarosites. The University will quantify the amount of H_3O^+ and H_2O in each series; low temperature i.r. will be the principal tool supported by Laser Raman spectroscopy where necessary.
- 4 - A complete materials balance will be obtained and the chemical information will be correlated with X-ray diffraction data available at CANMET.
- 5 - A few tests will be done in alkali-hydronium alunites ($M_x^+(H_3O)_{1-x}Al_3(SO_4)_2(OH)_6$) and the findings will be correlated to the corresponding jarosite compounds.
- 6 - All results of this study will be presented in a final report (10 copies) which will become the property of CANMET.

Experimental

A. Materials

Potassium Bromide (KBr)-The Harshaw Chemical Co.
Powder for pressed pellets.

Anachemica Perchloric Acid Fw. 100.46 1.764 gm/ml for 100% acid.

Distilled Water 0.9970 gm/ml at 25°C.

Liquid Nitrogen

Silica Gel: 400 mesh size

Jarosite samples supplied by CANMET:

Na J1790, Na J1789, Na J1788, Na J1787, Na J1786, Na J1773R, Na J1772R, Na J1793, Na Hk768R, Na J1767R, Na J1793, Na J1791, Na J1779, Na J1762R, J-308, Jar 168, J-326, J-281B, J-160, Lead Jarosite (J512), Mercury Jarosite, Rubidium Jarosite, Pb Jarosite (Chikuahua, Mexico), Ammonium Jarosite, Sodium Jarosite, Thallium Jarosite, Potassium Jarosite, Ammonium Jarosite "A", J470 Lead Jarosite, Beaverite, K Jarosite (Darwin Mine) Ag Jarosite, Lead Jarosite "Slow add".

B. Sample preparation

Jarosite samples were dried at 105°C for 24 hours then each sample was weighed by difference and transferred into 200 mg of KBr under dry nitrogen. After the pellet was pressed (6 tons/in²), the 13 mm diameter disc was mounted (in a dry N₂ atmosphere) to the cold finger of a liquid nitrogen cryostat.

The hydronium standard was prepared by adding a measured volume of perchloric acid to a weighed amount of dry silica gel. Next the mixture was vacuum dried to remove any excess water. To obtain a known amount of solid perchloric acid (H₃O⁺), a small portion of the acid/silica gel mixture was weighed and mixed into 200 mg KBr. This mixture was pressed into a pellet (6 tons/in²) so that an IR spectrum could be taken.

For the water standard, a known volume of water was introduced into a weighed sample of silica gel. Again, a weighed portion of this mixture was mixed with 200 mg of KBr and pressed into a pellet (6 tons/in²).

C. Infrared Spectroscopy

The IR spectra were recorded on a Perkin-Elmer 683 ratio recording spectrometer. Low noise and ordinate expansion allowed the recording of the weak signals in the jarosite compounds. All spectra were taken in the absorption mode so that direct correlation with concentration could be obtained. Microprocessor controlled functions on the spectrometer allowed the normalization of baselines in the spectra. This part of the experiment was carefully monitored since baseline anomalies can lead to larger errors in the final results.

D. Computer Data Analysis

After the spectra were obtained, a Hewlett-Packard Model 9836 micro-computer was used to analyze the data. First, the spectra were digitized with a digitizing graphics table. The procedure is to place the recorded spectra on the tablet and with a touch sensitive pen, trace the IR curve with successive applications of pen. A random number of points were obtained per spectra with subsequent normalization to 512 points.

Second, a fast fourier transform (FFT) method for spectral deconvolution was developed to enhance the resolution (see Figure 8). This technique was used with caution since over enhancement can lead to artificial results. The data analysis with the FFT technique increased the accuracy of the experiments which allowed one to obtain a reliable model of the spectral features.

Third, the computer program performed spectral averaging and baseline correction functions.

Results and Discussion

Recent literature indicates a low value for the amount of sodium present in sodium jarosites. The difference between the observed and theoretical amount of sodium is thought to be a deficiency due to the presence of hydronium and water in the lattice. The present work is to use the low temperature IR spectroscopic technique to determine the amount of H_3O^+ and H_2O in the lattice. We favor this technique over other spectroscopic methods because the analysis must be done on the sample without destruction. If the lattice is dissolved, then the origin of oxygen or water cannot be determined. Therefore, a discrimination between H_3O^+ and H_2O would be impossible.

The first task is to obtain a spectral assignment of the H_3O^+ and H_2O IR bands. In figures 1-5, we show selected IR spectra of hydronium-sodium jarosite solid solution series. In this series, the wt % of Na increases from 0.00% in sample Na J1790 to a maximum of 3.71% in Na J1762R. Additional information can be seen in Table I (supplied by CANMET). Since the existing literature on jarosites presents conflicting views as to the assignments in this spectral region, the present study endeavoured to extend the IR analysis so that a reliable band identification could be made.

In figure 1, the main spectral features are a weak band at 1575 cm^{-1} and a strong asymmetric band centered at 1640 cm^{-1} . Weak and strong are relative intensity strengths within the shown spectra. This spectral region $1500\text{ cm}^{-1} - 1800\text{ cm}^{-1}$ is weak with respect to the rest of the jarosite spectrum. Typical absorptions are approximately 0.05 absorbance units.

By surveying the spectroscopic literature, the 1640 cm^{-1} can be assigned to the H_2O bending vibration. At first, the band at 1575 cm^{-1} has the same vibrational frequency as the bending vibration of H_3O^+ in dehydrated perchloric acid ($\text{H}_3\text{O}^+ : 10_4^-$). In addition, the frequency of this band increases to 1590 cm^{-1} as the sodium content increases. Within this model, there are two species present (1) lattice water and (2) dehydrated H_3O^+ ions in the cationic site left vacant by the sodium ions. To test this model, a quantification of the 1575 to 1590 cm^{-1} has been attempted. The spectral intensities were measured against the dehydrated perchloric acid standard (1575 cm^{-1}) and the results are shown in column I of Table II. Two remarks can be made on the results: (1) the percentages are too high and (2) the amount of H_3O^+ is large for the 0.00% Na sample as expected with a continual decrease in H_3O^+ content until the last three samples. Here, the H_3O^+ percent increases. This observation is not expected and must reveal an error in the band assignment or standardization against an improper species. In column II of Table II, the H_3O^+ content is given with a hydrated perchloric acid sample as the standard. Although the percentages are lower, the trend in the amounts has not changed, consequently the new standard has not removed the anomaly. The only conclusion that can be made at this point is the failure of the two band model.

If the difference between the IR spectra of Na J1790 and Na J1762R is taken, one finds about twice as much water in the H_3O^+ jarosite (Na J1790). This information leads to the fact that the H_3O^+ in the samples is not dehydrated, and the vibrational frequency of hydrated H_3O^+ is not in the spectral region 1575 to 1590 cm^{-1} . Careful examination of the data shows a decrease of intensity in the 1700 - 1720 cm^{-1} region. This spectral domain

is consistent with hydrated acid IR spectra and is assigned to the bending vibration of H_3O^+ in an aqueous environment. Column III of Table II lists the percent of H_3O^+ in the samples using the intensity of samples at 1720 cm^{-1} . The standard used for these results was a hydrated HClO_4 /silica gel mixture in KBr. The frequency of the standard was 1740 cm^{-1} .

The remaining two bands (1640 cm^{-1} and $1575\text{--}1590\text{ cm}^{-1}$) can be assigned to water molecular in different environments. The band at 1640 cm^{-1} is probably ordinary lattice water since 1636 cm^{-1} is the average water frequency found in many hydrated crystals. If one inspects the literature for hydration data on cations, sodium and H_3O^+ ions have different hydration numbers reflection charge and size differences. As these ions are trapped in the lattice during precipitation, the water molecules of the first and may be the second hydration spheres are also trapped resulting in local water molecules, with different structures than bulk water. The hydronium ion can hydrogen bond to the water molecules next to it in the lattice site and lower the bending frequency to 1575 cm^{-1} . Likewise the Na^+ ion can influence the localized water molecules but not to the extent of H_3O^+ , and as a result, the frequency is closer to that of bulk water. This frequency is 1590 cm^{-1} . Columns IV and V of Table II give the intensities of these bands with respect to one mg of sample.

Conclusion

The results of the above analysis confirm a three band model of the H_3O^+ - H_2O IR spectral region for the bending vibration of the individual species. A quantitative analysis was not successful as reflected in the high percentages of H_3O^+ content. The only failure could be in the intensities of the standard (see Figure 7 for a typical spectrum). Here the H_3O^+ environment must be different than in the jarosite lattice. A similar argument must be applied for the H_2O content where values of 50% or greater are calculated. See Figure 6 for a sample, H_2O standard spectrum. Also, micro-Raman spectra were tried, but sample heating prevented the recording of valid data.

Table I

<u>Test</u>	<u>[Na₂SO₄]</u>	<u>wt% Na</u>	<u>% Fe</u>	<u>% SO₄</u>
Na-J-1790	0	0.00	36.11	36.88
Na-J-1789	0.005	1.08	34.46	39.88
Na-J-1788	0.007	1.07	34.20	39.67
Na-J-1787	0.008	1.32	34.21	40.03
Na-J-1786	0.01	1.48	34.15	40.15
Na-J-1773R	0.01	1.63	34.46	40.69
Na-J-1772R	0.015	1.91	34.26	40.81
Na-J-1783	0.03	2.24	33.83	39.85
Na-J-1768R	0.035	2.50	34.21	40.93
Na-J-1767R	0.04	2.81	33.75	40.93
Na-J-1793	0.06	3.00	33.28	41.28
Na-J-1791	0.08	3.19	33.16	41.17
Na-J-1779	0.10	3.51	33.88	40.99
Na-J-1762R	0.30	3.71	32.69	41.55

Table II

Quantitative Results of IR Studies

- Column I. Percent hydronium in samples based on the 1575 cm^{-1} intensity of the hydronium standard. The data are calculated from the intensity of the $1575\text{--}1590\text{ cm}^{-1}$ band in the samples.
- Column II. Percent hydronium calculated with both the hydrated and dehydrated hychromium standard. Sample band is the $1575\text{--}1590\text{ cm}^{-1}$ intensity.
- Column III. Data calculated with the hydrated hydronium standard (1720 cm^{-1}). Intensity of sample is taken at 1720 cm^{-1} .
- Column IV. Intensity (absorbance units/mg) of the water band divided by the sample mass. Bending vibration.
- Column V. Intensity (absorbance units/mg) of the localized water bending vibration.

Table II

Sample	I % H ₂ O	II % H ₂ O	III % H ₂ O	IV I ₁₆₄₀ /mg Sample	V I ₁₅₇₅₋₁₅₄₀ /mg Sample
NaJ1790	11.05	5.40	5.96	0.0446	0.0157
NaJ1789	11.11	4.94	4.24	0.0383	0.0114
NaJ1788	4.28	1.90	4.33	0.0382	0.0058
NaJ1787	5.89	2.62	5.19	0.0498	0.0048
NaJ1786	8.33	3.70	4.49	0.0421	0.0058
NaJ1773R	5.42	2.41	3.84	0.0361	0.0032
NaJ1772R	5.67	2.52	3.19	0.0277	0.0030
NaJ1783	6.19	2.75	2.72	0.0291	0.0034
NaJ1768R	5.59	2.48	1.48	0.0182	0.0033
NaJ1767R	4.58	2.04	2.43	0.0319	0.0040
NaJ1793	4.04	1.79	1.32	0.0233	0.0045
NaJ1791	11.59	6.44	0.826	0.0147	0.0042
NaJ1779	11.87	5.27	0.306	0.0283	0.0047
NaJ1726R	12.49	5.55	0.117	0.0167	0.0046
J-308	14.44	6.42	2.28	0.0371	0.01146
Jar 168	12.12	4.29	2.83	0.0271	0.00743
J-326	9.03	4.05	2.28	0.0185	0.0049
J-281B	13.28	5.90	1.76	0.0306	0.01088
J-160	0.0	0.0	2.54	0.0261	0.0
Lead Jarosite J512	18.30	8.13	1.18	0.0216	0.00927
Mercury Jarosite	18.8	4.72	0.269	0.0288	0.00932
Rubidium Jarosite	0.0	0.0	1.99	0.0302	0.0
Pb Jarosite (Chihuahua, Mexico)	0.0	0.0	0.550	0.0314	0.0
Ammonium Jarosite	?	?	?	0.0049	?
Sodium Jarosite	18.28	6.06	2.16	0.0224	0.1293
Thallium Jarosite	0.0	0.0	0.813	0.0209	0.0
Potassium Jarosite	0.0	0.0	2.18	0.0355	?
Ammonium Jarosite "A"	?	?	?	0.0151	?
J470 Lead Jarosite	0.0	0.0	2.66	0.0286	0.0
Beaverite	15.39	8.54	0.604	0.0190	0.0099
K Jarosite (Darium Mine)	?	?	?	?	?
Ag Jarosite	7.74%	3.44	0.265	0.0184	0.0064
Lead Jarosite "Slow add"	12.99%	5.77	4.60	0.0382	0.0083

FIGURE 1 NA-J-1790

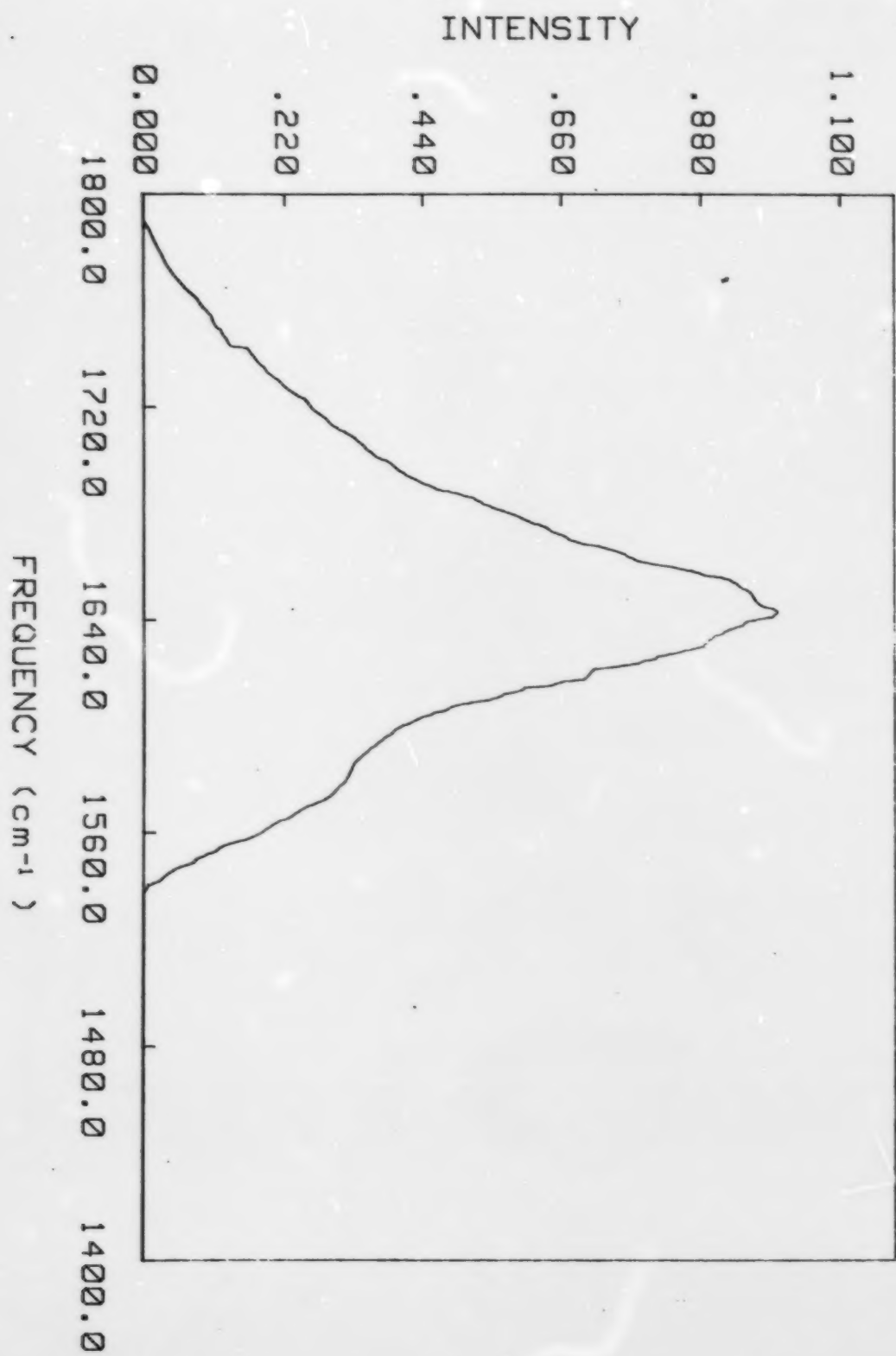


FIGURE 2 NR-J-1787

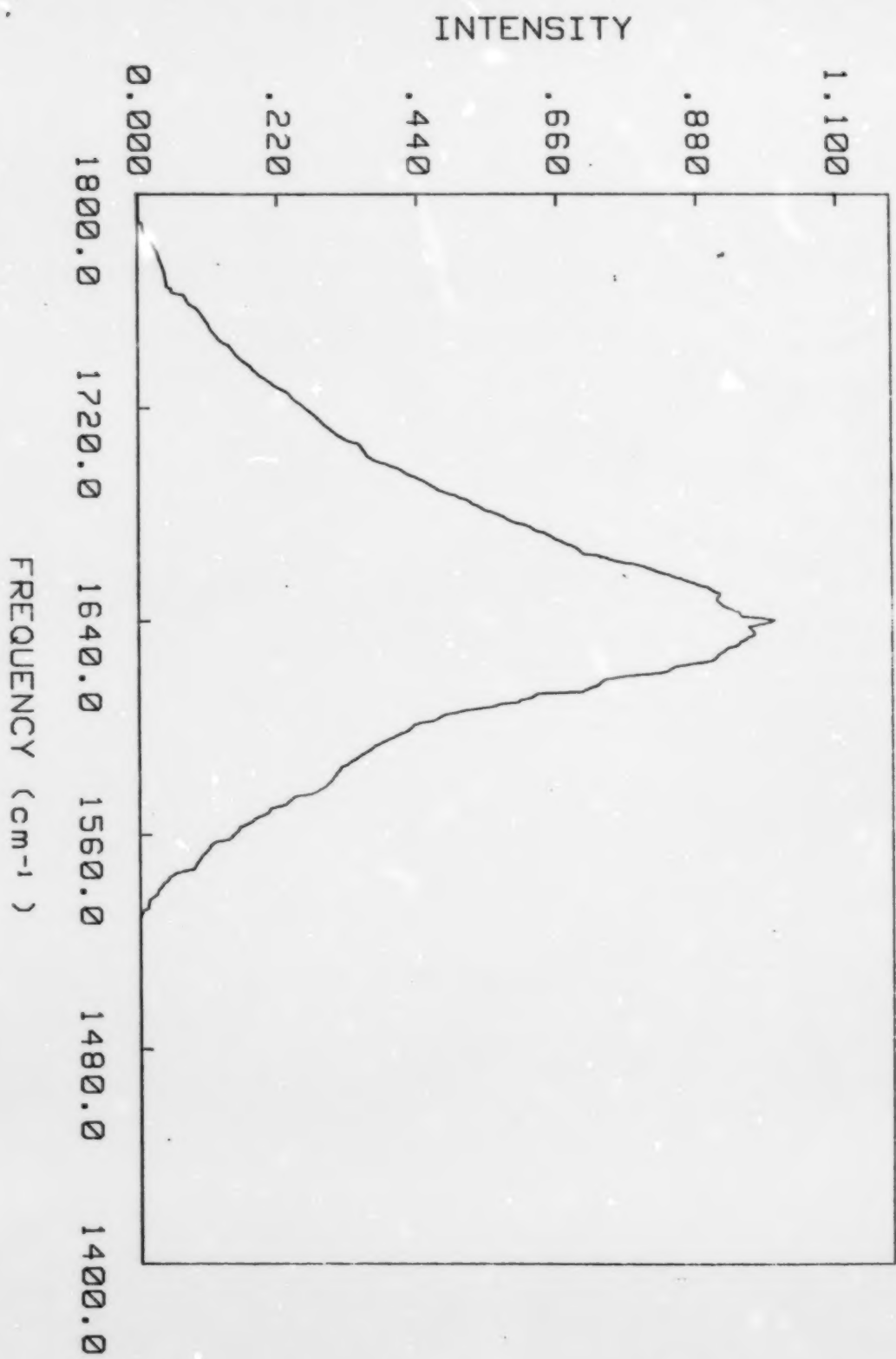


FIGURE 3 NA-J-1772R

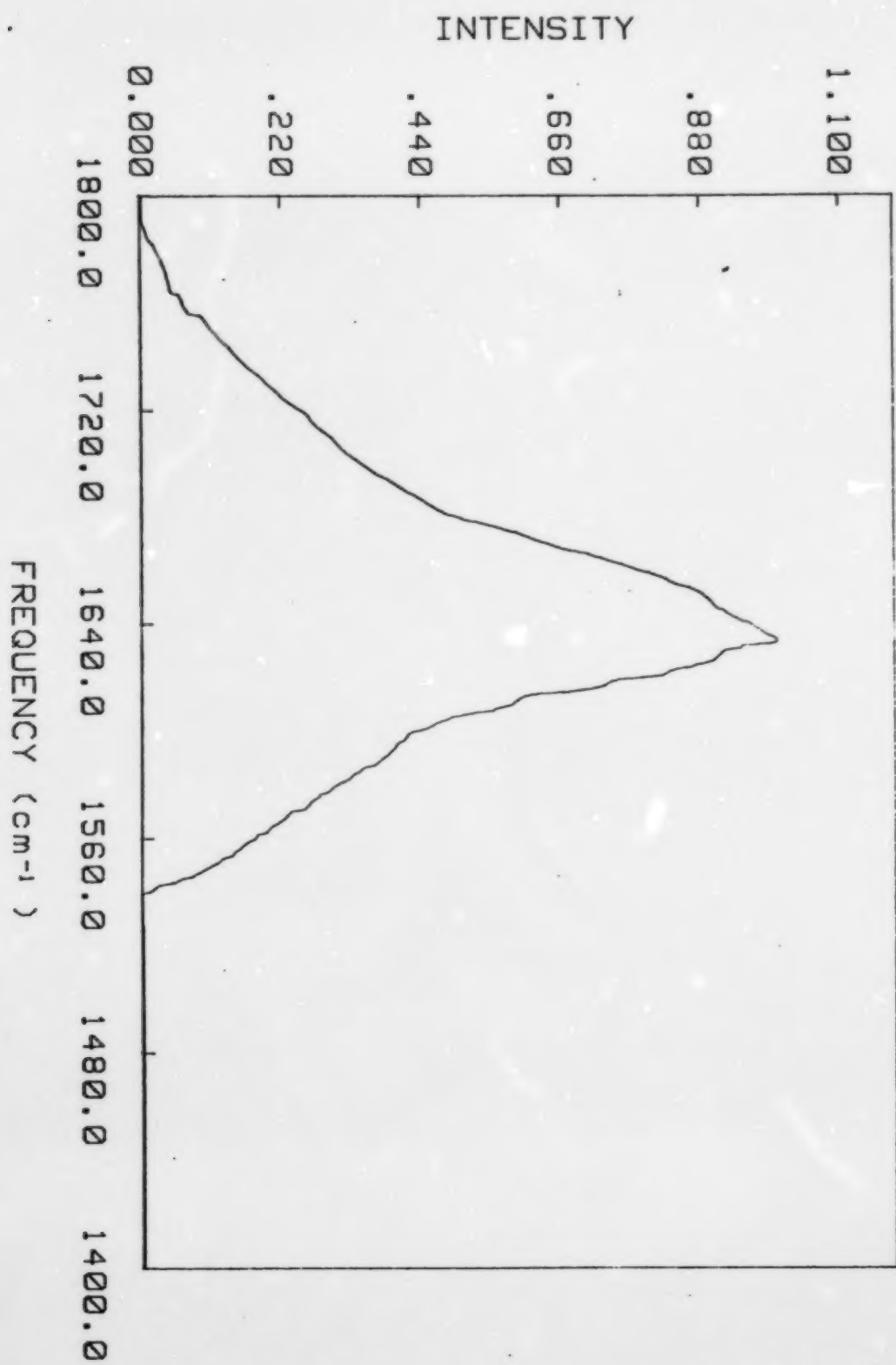


FIGURE 4 NA-J-1793

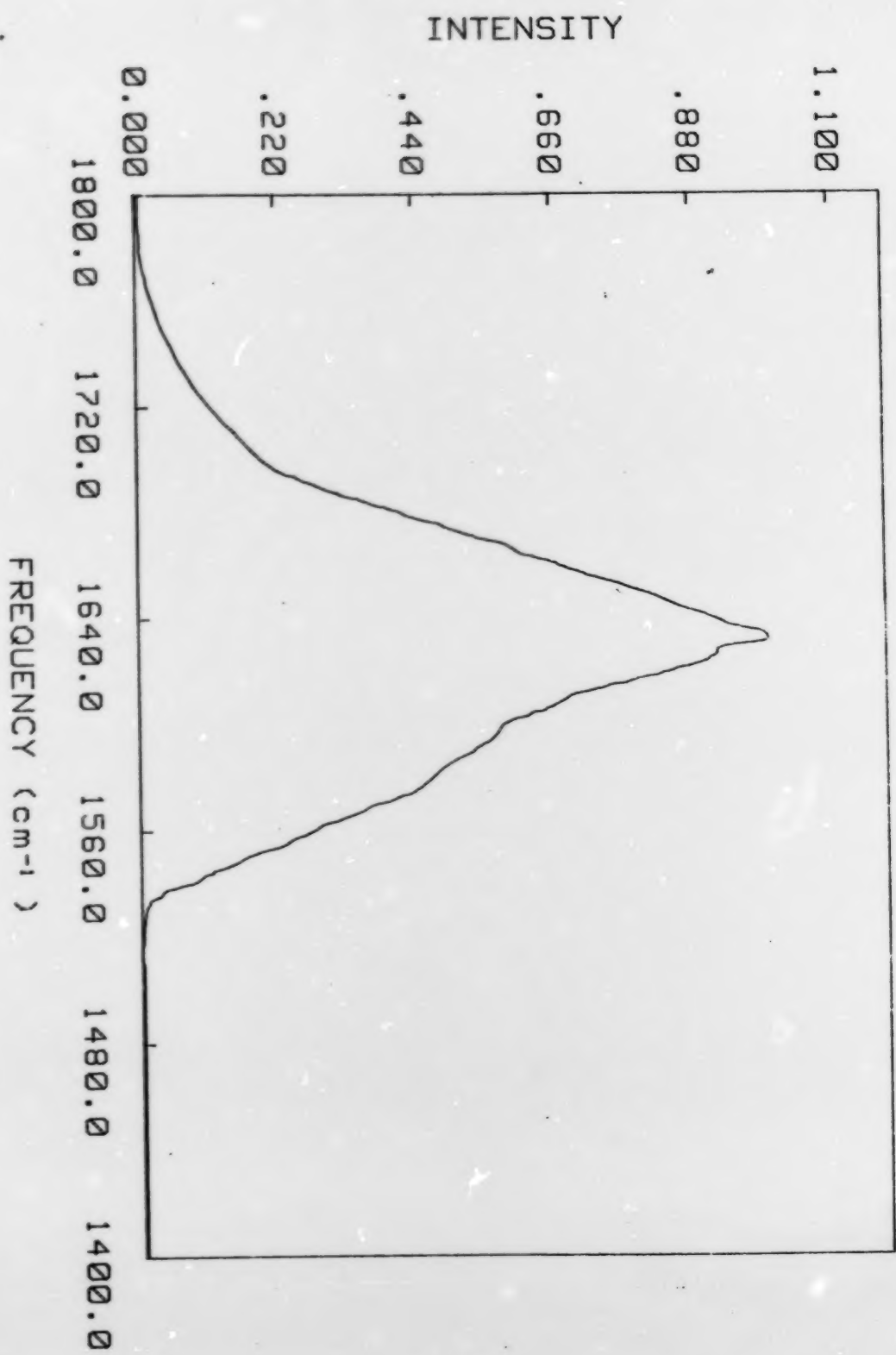


FIGURE 5 NA-J-1762R

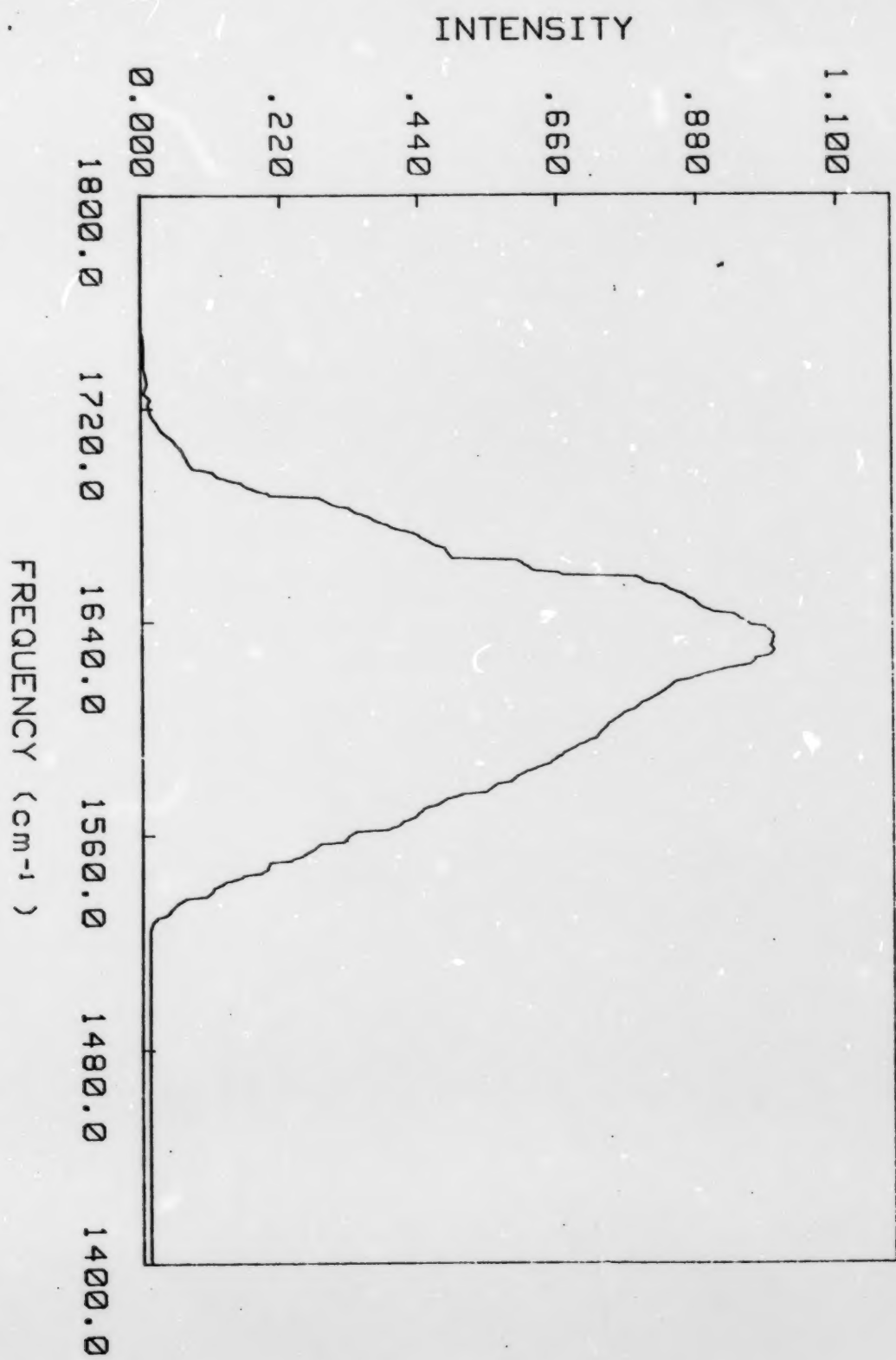


FIGURE 6 H₂O STANDARD

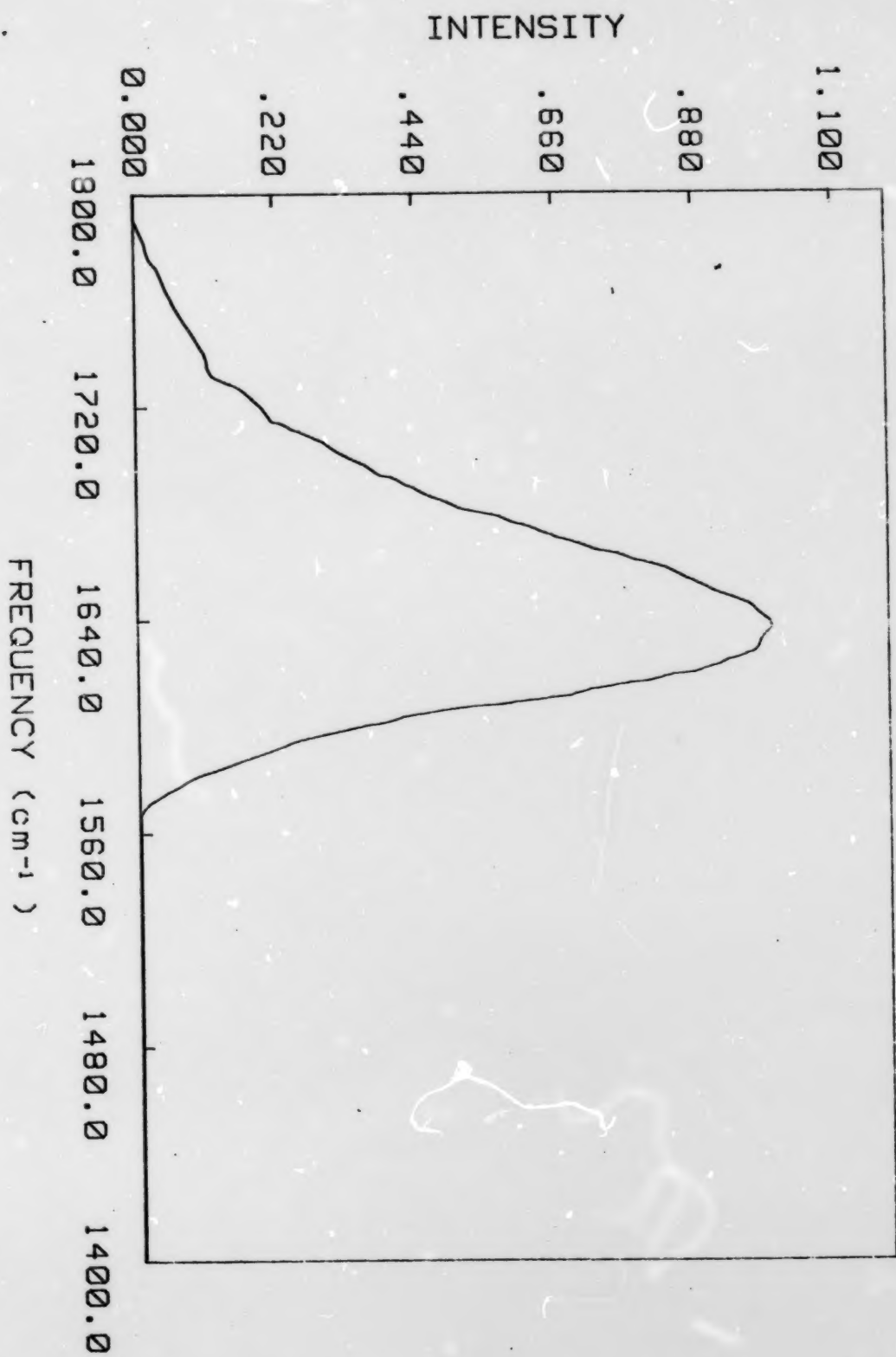


FIGURE 7 H3O STANDARD

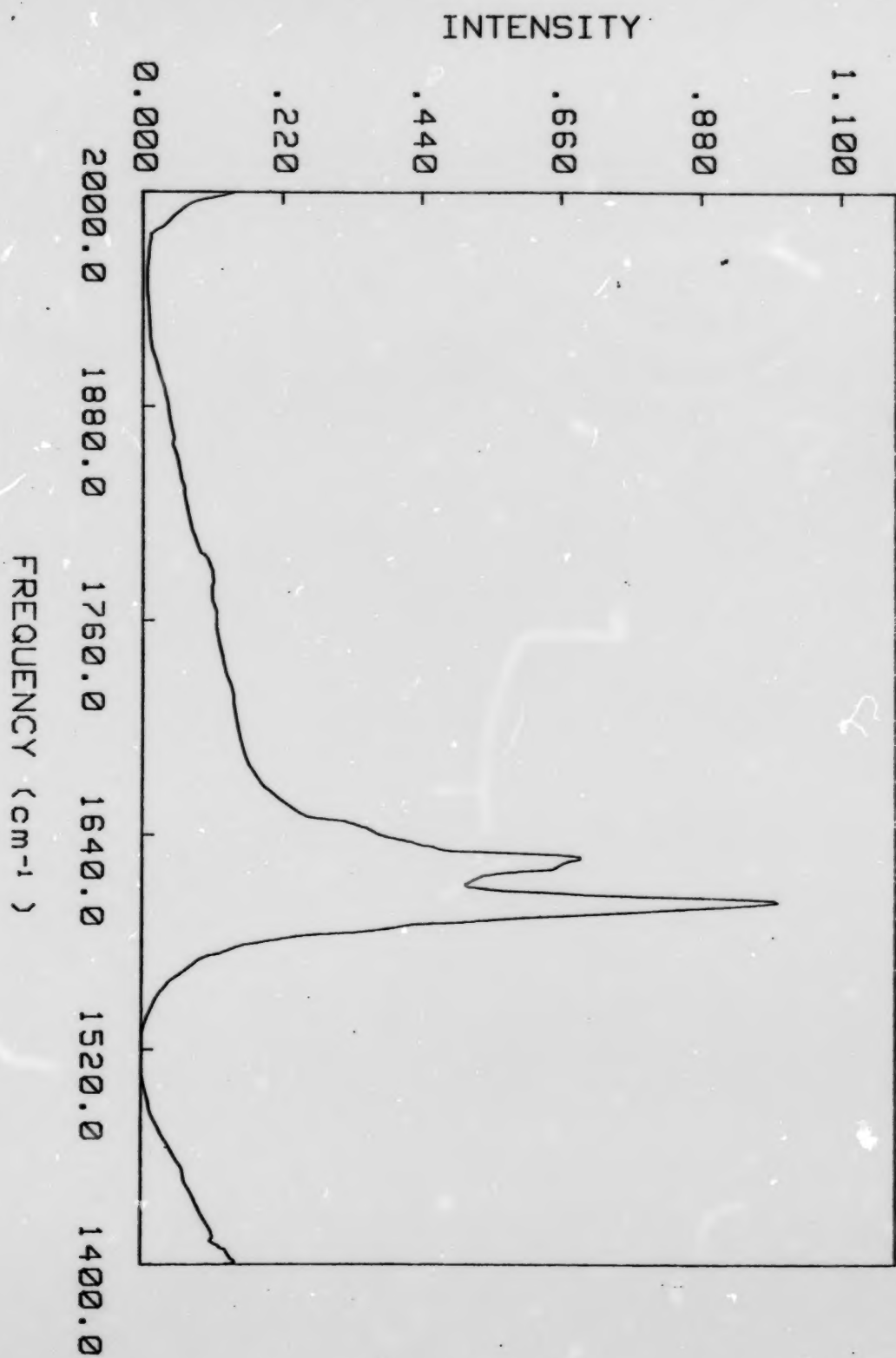
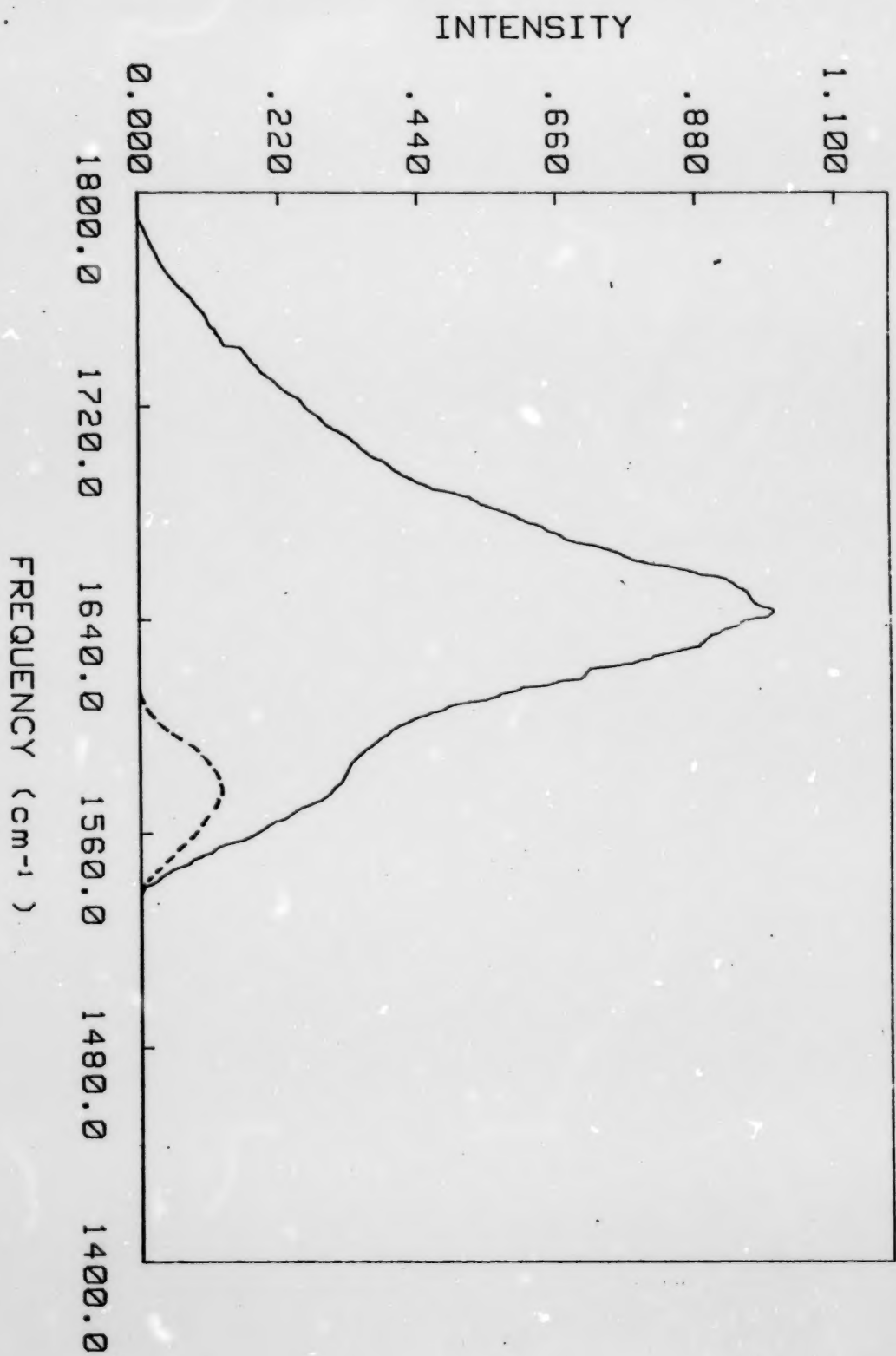


FIGURE 8 NA-J-1790 DECONV



POOR

QUALITY

ORIGINAL